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## **Adhesion concepts in dentistry: tooth and material aspects**

Özcan, Mutlu ; Dünder, Mine ; Erhan Çömlekoğlu, M

**Abstract:** Adhesion concepts require understanding of substrate material properties, surface conditioning methods and chemical interactions, formation of interfaces/interphases between different material combinations, changes at interfaces with time, failure mechanisms and failure modes of the interfaces as a consequence of aging phenomenon. In dentistry, different methods are being used to test adhesion of resin-based materials to various biological and artificial substrates that require individual conditioning protocols. Variations among specimen configurations, material properties and chemical compositions of adhesives, test methods and test conditions all have effect on adhesion of similar or dissimilar substrates. Selection of the test, its proper execution, as well as the interpretation of the data through chemistry of the materials involved is of importance. Although adhesion to enamel is not a major concern today, effective adhesion to dentin requires several steps where failure in any of these consecutive events might result in failure of the whole system after long-term clinical use. Test methodologies used for assessment of mechanical behavior of materials in engineering may not directly apply to tooth-material combinations in dentistry. The objective of this review on adhesion in dentistry is to summarize current materials and methods used in dental materials testing and to summarize the current state-of-the-art in adhesion durability and quality with respect to the material type.

DOI: <https://doi.org/10.1080/01694243.2012.691038>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-75611>

Journal Article

Accepted Version

Originally published at:

Özcan, Mutlu; Dünder, Mine; Erhan Çömlekoğlu, M (2012). Adhesion concepts in dentistry: tooth and material aspects. *Journal of Adhesion Science and Technology*, 26(24):2661-2681.

DOI: <https://doi.org/10.1080/01694243.2012.691038>

## **Adhesion Concepts in Dentistry: Tooth and Material Aspects**

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***Running Heads:*** Review on Adhesion in Dentistry

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## **Abstract**

Adhesion concepts require understanding of substrate material properties, surface conditioning methods and chemical interactions, formation of interfaces/interphases between different material combinations, changes at interfaces with time, failure mechanisms and failure modes of the interfaces as a consequence of aging phenomenon. In dentistry, different methods are being used to test adhesion of resin based materials to various biological and artificial substrates that require individual conditioning protocols. Variations among specimen configurations, material properties and chemical compositions of adhesives, test methods and test conditions all have effect on adhesion of similar or dissimilar substrates. Selection of the test, its proper execution, as well as the interpretation of the data through chemistry of the materials involved is of importance. Although adhesion to enamel is not a major concern today, effective adhesion to dentin requires several steps where failure in any of these consecutive events might result in failure of the whole system after long term clinical use. Test methodologies used for assessment of mechanical behaviour of materials in engineering may not directly apply to tooth-material combinations in dentistry. The objective of this review on adhesion in dentistry is to summarize current materials and methods used in dental materials testing and to summarize the current state-of-the-art in adhesion durability and quality with respect to the material type.

## **Keywords**

Adhesion, adhesives, biodegradation, bond strength testing, ceramics, composites, metals, minimal invasive dentistry

## 1. Introduction

Adhesion constitutes the attraction between similar or dissimilar materials by several mechanical and physical processes and intermolecular forces. The adhesive interface comprises an “adhesive” that is placed on a “substrate (adherend)”. When an adhesive is used to attach one substrate to the other, two interfaces are formed between the adhesive and the substrates [1]. Without any adhesion promoter, although physical as well as chemical adhesion is present in all dental material applications, the resultant bond strength is weak or negligible when compared to mechanical bonding. Mechanical interlocking of the adhesive into the substrate irregularities contributes the most to the bond strength at the interface in almost all situations [2,3].

In most of the dental applications, two different substrates are bonded with an adhesive. The adhesive has to seal the interface between the cavity and the restorative material, thus reducing the risk of leakage, post-operative sensitivity, marginal staining and recurrent caries [4]. Adhesion in dentistry has two aspects, namely the adhesion to tooth and the restorative material where the quality of adhesion varies depending on the tooth and material properties. Therefore the aim of this article is to review the current information concerning these aspects. From the dental perspective, there are numerous substrates such as enamel, dentin, cement, post-core, remaining dental amalgam on tooth or a dental implant abutment, dental composite resin, cast or all-ceramic inlay/onlay/crown, veneer, resin-bonded fixed dental prosthesis or an orthodontic bracket.

### *1.1. Developments in the Field of Adhesion in Dentistry*

Some fifty years ago, clinicians had to drill extensively not only the infected but also the healthy tissues to obtain mechanical retention for the restorative materials [5].

One of the leading innovations of recent times is the discovery of enamel and dentin etching with phosphoric acid that was first introduced by Buonocore [6]. With this phenomenal discovery, it has become possible to adhere synthetic resins to the tooth tissues. The rationale behind this requirement is that the loss of tooth substance by caries or trauma cannot be repaired by living materials and, therefore, should be restored by synthetic materials.

From the restorative materials perspective, the popularity of chemically cured dental methacrylates diminished during the mid-1950s due to their poor physical properties and negative effects on pulp tissue that stem from polymerization shrinkage and monomer leaching [7]. Polymerization here, refers to the cross-linking of monomers to form long chain polymers to improve material strength where contraction stresses cannot be avoided. Bowen improved the mechanical and adhesive properties of resinous restorative materials using epoxy resin (diglycidyl ether of bisphenol A) mixed with silica particles [8]. However, the resin was initially not ideal as the presence of moisture compromised the polymerization process of the epoxy resin. Bowen converted epoxy resin to a dimethacrylate by linking methyl methacrylate groups to the epoxy resin [9]. A mixture of silicon dioxide, boron oxide, aluminum oxide, or strontium oxide particles was used in this formulation. The resultant resin was called 2,2' - bis-[4-(methacryloxypropoxy)-phenyl]propane (bis-GMA), or "Bowen's resin" [7]. This resin matrix is usually cured by photoinitiated free radical polymerization. bis-GMA is one of the most commonly used monomers. Since bis-GMA resin is highly viscous, a low viscosity monomer, such as tri(ethylene glycol)dimethacrylate (TEGDMA), is usually added to the resin. Today, the bis-GMA/TEGDMA system is one of the most widely used dental resin systems. The function of bis-GMA is to limit the volumetric shrinkage induced by

photopolymerization and to enhance resin reactivity, while TEGDMA provides for increased degree of conversion [10]. During the synthesis of bis-GMA monomer, iso-bis-GMA monomer is produced as a by-product.

The combination of bis-GMA based resins with the acid-etching technique led to new perspectives in dentistry. Adhesion concept shifted from macro-mechanical to micro-mechanical and surface chemistry approaches and this provided new treatment possibilities in orthodontics and minimally invasive interventions.

### *1.2. Minimally Invasive Dentistry*

Operative treatment concepts can be based on non-invasive, minimally invasive or invasive strategies using various materials. Dentistry utilizes a variety of materials ranging from polymers, metals and metal alloys to resin based composites and ceramics for restorative procedures. Developments in polymer and ceramic fields have largely eliminated the use of metals and thus have reduced the possible corrosion products in the mouth.

Since polymeric, ceramic or metallic materials present different material properties and preparation techniques for their application that may vary from non-invasive to minimal, moderate or more invasive treatment options, from the ethical point of view it is almost impossible to conduct clinical trials to compare different treatment modalities or materials in the same mouth. Despite all the recent developments, no material to date is flawless. Survival rates of restorative materials inevitably decrease over years.

Adhesion to enamel and dentin is not a clinical concern anymore after the discovery of acid etching and adhesives. Dental composite resin materials are cost-effective and less invasive compared to other available materials and their direct intraoral applications are routine. Current problems for direct composite resin

applications are rather related to the hydrolytic instability of adhesives and shrinkage-related problems after composite resin polymerization and its consequences such as internal cracks in the composite, shear forces directed to cusps thus causing possible cusp fractures, microleakage through the margins of the composite restorations, which can cause caries and pain. The dilemma in the dental profession is the choice between the polymeric materials versus dental ceramics (feldspathic, glass and oxide ceramics) in minimally invasive applications. If ceramic materials are to be chosen over resin composites, evidence-based studies should be evaluated with caution [11,12]. In a clinical study conducted at a university, 28% of glass-ceramic laminate veneer restorations (0.5-0.8 mm in thickness), a minimally invasive treatment modality, needed repair after 10 years, indicating that refinishing, repolishing or repair of chipping and fracture using composites was necessary. On the other hand, practice-based evidence reported that 53% of glass-ceramic laminates survived without re-intervention for 10 years. These two studies clearly emphasize the need for optimization of the materials and the application techniques.

### *1.3. Classification of Dental Adhesive Systems*

In order to achieve a stable bonded interface to dental tissues, adhesive systems have to include three crucial application steps, i.e. etching, priming and bonding. Etching with an acidic solution, such as 35-37% orthophosphoric acid, demineralizes both enamel and dentin surfaces producing roughness and increasing their surface free energy [4]. With priming, wettability of the tooth surface is increased and hydrophilic monomers and solvents in the primer composition provide substitution of the water on the substrate with the resin monomers. In the bonding step, after penetration and polymerization of monomers into the etched enamel surface or exposed collagen network in dentin, micromechanical interlocking occurs [4]. Even

though all adhesives possess etching, priming and bonding abilities, their compositions, contemporary adhesive systems are named as: etch-and-rinse, self-etch, and self-adhesive, based on the number and combination of the steps used in the system [13,14]. Self-etching refers to the acid etching and priming of dentin at the same time with acidic monomers without rinsing resulting in a modified smear layer to form the hybrid layer between the dentin and resin, whereas etch-and-rinse approach refers to acid etching of the enamel/dentin surfaces and after this treatment the surfaces are rinsed in order to eliminate the smear layer and then primer, bond and resin application to form the hybrid layer [11].

The etch-and-rinse approach can be further divided into two subgroups of 3-component and 2-component systems. While the former one is characterized by the sequential and separate application of etching, primer and bonding agent, in the simplified 2-step approach, the primer and bonding agent present in a single bottle are applied on the tooth surface immediately after removal of etching material [15,16].

The major complication for the etch-and-rinse systems is the potential incomplete penetration of resins into exposed collagen mesh [16-19]. In order to overcome this problem self-etch adhesives have been improved. With the self-etch adhesives, acidic monomers (self-etching primer) that simultaneously demineralize and prime tooth surfaces are applied and dried on the tooth surface. Then, a bonding agent from a separate bottle is used. These systems can also be further divided into subgroups based on their self-etching capacity; strong ( $\text{pH} < 1$ ), intermediately strong ( $\text{pH} \approx 1.5$ ), mild ( $\text{pH} \approx 2$ ), and ultra-mild ( $\text{pH} \geq 2.5$ ). The arbitrary pH scale depends on the substrate to be treated. When working on enamel surface, intermediately strong to mild and for dentin surfaces mild to ultra-mild acids are used. Bonding



agent is a flowable, less inorganic content bearing resin that is applied as an intermediate layer before composite resin application [13].

Taking the self-etch approach one step further, one-component, so-called 'self-adhesive' systems have been developed. With this technique, acidic monomers (esters generating from the reaction of a bivalent alcohol with methacrylic acid and phosphoric/carboxylic acid derivatives) that etch, prime, and bond simultaneously are applied on the tooth surface as a single solution. These monomers possess functional acidic groups to demineralize hard tissues and copolymerize with bonding resins sequentially [16-19]. Self-etch adhesives contain specific functional monomers which determine their adhesive performance.

## **2. Adhesion to Dental Tissues**

For better understanding of surface reactions of the current bonding systems with dental hard tissues, a brief discussion regarding tooth substrates would be helpful. While a tooth can be divided macroscopically into 2 fragments i.e., as a crown and a root, its structural composition consists of three hard tissues: enamel, dentin and cementum. Enamel that covers the crown is completely acellular and it is the most mineralized hard tissue in the body. The other outer part of the tooth is cementum by which the root is totally covered. The third hard tissue, dentin, underlies the enamel and cementum layers and forms the bulk of the tooth [20,22].

### ***2.1 Adhesion to Enamel***

Compositionally, enamel consists of 96% inorganic hydroxyapatite crystallites  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$  by weight, the rest of the matrix being water (4%) and proteins (collagens) (1%) [22]. Structural form of enamel is characterized by a higher order structure that consists of rods that are organized in a repetitive pattern [23].

While micromechanical retention of resin tags on roughened surfaces is still the best bonding mechanism on enamel [4,6], chemical bonding to hydroxyapatite can also be accomplished through chelation reaction with the calcium ions or with the phosphate or the hydroxyl groups [24]. For the micromechanical adhesion, demineralization of the surface enamel layer is required and the multi-step etch-and-rinse approach with highly concentrated phosphoric acid (35-37% by weight, pH=1.0) is regarded as 'gold standard' for this purpose. Acid etching of enamel selectively dissolves enamel rods and provides micro-roughness on the surface with increased surface energy that is essential for micromechanical adhesion [25]. Several etching agents such as maleic, citric, phosphoric, and nitric acid with different concentrations have also been tried on enamel. However, phosphoric acid is apparently preferred due to its known advantage in efficiently etching enamel to an operator identifiable frosty appearance known for good adhesion to enamel [26]. When the surface topography is created on the surface, the monomers in primers and bonding agents can penetrate into the porous substructure to form extensions (tags) at the enamel-restoration interface, become polymerized and with the application of subsequent resin layers micromechanical interlocking which provides most of the bond strength is provided. The *in vitro* shear bond strength of composite and luting resins to etched enamel has been reported to vary from 17.7 to 49.2 MPa depending on the test method and aging (thermocycling) conditions used, corresponding approximately to 5 years clinical service. The results revealed mostly interfacial failure between the composite and/or luting resins and etched enamel [27-30].

With the self-etching technique, an acidic monomer is used to demineralize enamel surfaces. Self-etching primers with lower pH values can etch enamel surface more aggressively. On the other hand, milder systems can provide a better etching

pattern [31]. Both on intact and ground enamel, higher bond strength values can be achieved with etch-and-rinse systems compared to self-etching systems [32-34].

Besides micromechanical bonding, chemical interaction between resin and enamel apatite can occur through the treatment of enamel by polyalkenoic acids. This occurs through ionic bond formation between the carboxyl groups of the polyalkenoic acid with calcium of hydroxyapatite [34]. Thus, the chelation of carboxyl groups that are derived from polyalkenoic acid with the calcium in apatite can be obtained as represented below:



The use of polyalkenoic acids clean and roughen the enamel surface but the long-term durability of the achieved bond strength is still not ideal [34,35].

## *2.2 Adhesion to Dentin*

Dentin is a tissue with physical and chemical properties that resemble that of bone. It is 70% mineralized with hydroxyapatite crystals and its organic phase, about 20% by weight, is mostly collagen while the remaining 10% is water. The water in dentin is trapped in the collagen fibers during dentin formation and this is bonded to hydroxyproline ends inside the collagen fibers [35-37]. Morphologically, dentin contains dentinal tubules, formed by the deposition and mineralization of a predentin matrix. The permeability of this tissue is a direct consequence of the presence of tubules [38]. Between the tubules the intertubular dentin is composed of a dense matrix of collagen fibrils, ranging from 50 to 200 nm in diameter, surrounded by hydroxyapatite mineral and the more mineralized peritubular dentin immediately adjacent to the tubules contains less collagen. Type I collagen, the most abundant collagen of the human body, accounts for 90% of the total protein in the organic matrix of bone and dentin [38].

It has been demonstrated that the nucleated apatite crystals grow mineral platelets that are highly organized within the collagen fibrils [39]. Type I collagen matrix does not have the capacity to induce matrix-specific mineral formation. Ordered mineralization of apatite on collagen fibrils has been shown to require additives such as phosphoproteins, glycosaminoglycans and proteoglycans. Therefore, the non-collagenous proteins (NCPs) that are tightly bound to the collagen fibrils in mineralized tissues are important for understanding the mechanism of hybridization and mineralization. Bone and/or dentin-specific NCPs are mostly acidic in nature and are rich in glutamic acid, aspartic acid, and phosphoserines. They possess high calcium binding capacity and hydroxyapatite affinity. *In vitro* mineralization analyses suggest that these NCPs can greatly influence the apatite deposition rate and morphology of crystals, thus they can be considered as nucleators or inhibitors of mineralization [40].

Bonding of 4-methacryloxyethyl trimellitate anhydride together with tri-n-butyl borane in the presence of poly(methyl methacrylate) (4-META / PMMA TBB resin) to dentin via hybridization of impregnated monomers was first described by Nakabayashi *et al*, in 1982 [41]. The mechanism of bonding by hybridization applies to almost all bonding systems. Etching dentin removes the smear layer and the hydroxyapatite mineral phase from the tissue surface, creating a network of exposed collagen fibrils as the underlying substrate. The hybridization process is achieved by the infiltration of the primer into the open spatial network in the collagen matrix exposed by dentin demineralization, and its polymerization. Hybrid layer formation on the surface and within the subsurface of dentin depends on both the permeability of dentin and the diffusion of applied monomers [15,41]. Due to the hydrophilic nature of the matrix, Nakabayashi *et al*. [41] proposed that a methacrylate with both hydrophilic

and hydrophobic groups could improve the diffusion of a monomer mixture and enhance its impregnation into appropriately conditioned dentin substrates. The hydrophilic groups may facilitate permeation of the monomer into the collagen matrix leading to the formation of a collagen-resin hybridized layer. This procedure significantly improved bonding and sealing at the resin-dentin interface [42,43]. The bond strength of composites and luting resins to dentin varies over a wide range depending on the adhesive system used, type of materials bonded and test methodologies. However, due to the ultrastructure at micro and/or nanolevel and collagen-rich composition of the dentin tissue, bond strength to dentin is lower than that to enamel.

As the structure of bulk and surface dentin are different, the resin-dentin bonding mechanism changes. While the dentin surface is dominated by intertubular dentin, the bulk dentin is dominated by dentin tubules. Therefore, the bonding mechanism depends on dentin tubules in bulk dentin and on intertubular dentin in dentin surface [44-47].

It has been observed that leaving the conditioned dentin slightly moist by mild air drying the dentin surface during bonding improved the bond strength, and this procedure became identified as '*wet bonding*' to dentin [48]. Drying of dentin exposed after acid demineralization may lead to a volume change, which is described as the structural collapse of the collagen matrix that results in incomplete penetration of monomers into the matrix. The prevention of collapse is made possible by maintaining conditioned dentin in the wet state [49,50]. In wet bonding, the monomer replaces the water within the exposed collagen scaffold. Thus hydrogen bonding, van der Waals, and electrostatic interactions between the monomer and the collagen molecules (proteoglycans, glycosaminoglycans and phosphoproteins) may be

facilitated. Therefore, both monomer and solvent molecules should be compatible with the moist environment of the collagen matrix. Hydrophilic resin monomers are often dissolved in volatile solvents, such as acetone and ethanol. The inclusion of these volatile solvents helps in the displacement of water from the dentine surface, easing penetration of the resin monomers into the microporosities of the exposed, acid-demineralized collagen network [51]. In order to form an effective hybrid layer, hydrophilic monomers carried in water, ethanol, or acetone, are used as primers [25]. Following primer/bonding agent application, carrier solvent is evaporated by slight air drying, leaving the resin material within the collagen mesh. The bonding agent co-polymerizes with the primer, a base material for wetting the dentin surface and easing further penetration of the monomers. Some commonly used comonomer blends resin restorative composites or in resin based luting agents are: bis-GMA: bisphenol A diglycidyl ether dimethacrylate; bis-GMA-E: ethoxylated bisphenol A diglycidyl ether dimethacrylate; CQ: camphorquinone; EDMAB: ethyl N,N-dimethyl-4-aminobenzoate; HEMA: 2-hydroxyethyl methacrylate; DMABA: dimethylaminobenzoic acid; TEGDMA: triethyleneglycol dimethacrylate; TCDM: di(hydroxyethylmethacrylate) ester of 5-(2,5-dioxo tetrahydrofurfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride [52]. Ideally, all solvents and water should be completely eliminated from the adhesive before light-curing of the resin, as they may have an adverse effect on polymerization of the adhesive resin monomers. This is achieved by allowing an evaporation time between application and curing of the adhesive resin. However, the monomer to water ratio increases as water evaporates from the adhesive and lowers the vapour pressure of water, reducing the ability of water and solvents to evaporate from the adhesive. It is likely that residual water and solvent will be trapped within the adhesive resin upon curing and this may

compromise the overall bonding and the mechanical properties of the cured resin [53].

Acidic etchants remove the mineral phase of the dentin layer depending on the individual dentin quality, quantity and applied pH, but the collagen component is not totally dissolved by phosphoric or citric acids [54]. Resin diffusion into and within the demineralized intertubular dentin matrices occurs via 20-30 nm wide interfibrillar spaces. These narrow interconnecting channels contain noncollagenous macromolecules such as proteoglycans, proteins, and glycosaminoglycans that remain within the matrix and decrease monomer permeability after acid conditioning of the dentin [54,55]. Therefore, to avoid collagen collapse and maintain large interfibrillar spaces permitting monomer diffusion within the exposed collagen mesh, etch-and-rinse systems should be applied on wet dentin [48].

First adhesive approach for dentin bonding was etch-and-rinse technique. Thereafter, self-etch and self-adhesive systems became widespread. Regardless of the number of steps involved, the complete diffusion and interaction of the hydrophilic monomer within the porous tissue substrate to form a hybrid layer at the tissue-resin interface was found to be the key factor in durable dentin-adhesive bonding [55]. The primer and bonding agents contain a mixture of resin monomers and initiators with light-, chemical- or dual- curing modes and some other additives. The priming agents consist of hydrophilic monomers that can be copolymerized with the methacrylate monomers used in restorative applications. On the other hand, self-etching primers are characterized by the hydrophilic monomers of acidic nature to etch the mineralized tissue. However, monomers in the self-adhesive systems are more acidic (pH=1) than those in self-etching systems (pH 1.9-2.4). Self-adhesives use acidic bonding agents that contain methacrylate phosphate esters or methacrylate

carboxylate esters with non-reactive fillers [15,56]. Unlike etch-and-rinse systems, multifunctional phosphoric acid methacrylates in self-etch and self-adhesive systems chemically react with the hydroxyapatite of the hard tooth tissue (dentin) through adsorption of the acid anions onto hydroxyapatite and covalent bond formation [57].

### *2.2.1 Biodegradation*

Biodegradation of the non-encapsulated collagen fibrils that are the main cause of degradation of the hybrid layer and thus of adhesion between the tooth and the restoration [54]. Biodegradation occurs in the hybrid layer *in vivo* and involves consecutive processes. The first stage of biodegradation begins when dentin is acid-etched for removal of the smear layer, exposing the underlying collagen fibril matrix for hybrid layer formation. The second stage involves extraction of the resins that had infiltrated the dentin matrix through water-filled nanometer-sized voids within the hybrid layer. The third stage involves enzymatic attack of the exposed collagen fibrils, leading to depletion of collagen fibrils [16]. It has been demonstrated that exposure of collagen matrix by acid etching activates matrix metalloproteinases (MMPs) [58], that are known to cause collagenolysis in the presence of water. The trend in current research has, therefore, shifted to the recovery of exposed (denuded) collagen fibrils. However, the mechanism regarding the origin of initiation of biodegradation in the hybrid layer is complex. Incomplete penetration of resin into exposed collagen matrix as well as intrinsic enzymatic activity in the dentin result in resin-dentin bond breakdown. However, from which side of this trilayered complex (adhesive- hybrid layer-dentin) the degradation begins remains unclear. Fundamental research in this area would help the researchers to reinforce this site, thereby maintaining or enhancing the durability of the bonded interfaces.



Breakdown of the inorganic polymer phase within the adhesive and the hybrid layers or collagen fibrils in the hybrid layer (between the dental tissues and the adhesive-primed and conditioned-) may cause degradation. Hydrolysis, which is a chemical process that breaks covalent bonds between the polymers by addition of water to ester bonds (methacrylate phosphate esters or methacrylate carboxylate esters with non-reactive fillers) results in loss of the resin composite mass over time. As a consequence, resin degradation within the hybrid layer occurs [59]. Incompletely cured adhesive resin or ester groups in the polymer chains within the adhesive or hybrid layer due to inadequate monomer impregnation into wet dentin substrate, result in lower degree of polymerization of adhesive resin as well as salivary enzymes are reported to cause hydrolysis [60]. As the resin degradation is related to water sorption within the hybrid layer, the degree of water sorption of self-etch adhesives has been studied [61,62]. The acidic groups reacting with the main inorganic component, which is hydroxyapatite, of the dental hard tissue form ionic bonds.

With the incorporation of hydrophilic and ionic resin monomers into the bonding agent in self-etch adhesives, no hydrophobic resin layer can be formed at the bonded resin-dentin interface, irrespective of the etch-and-rinse or the self-etch strategy. This leads to the creation of hybrid layers permitting movement of the water present in the dentin as a consequence of dentin's 10% water content by weight throughout the bonded interface even after the adhesive is polymerized [63]. Resin adhesives containing more acidic hydrophilic monomers, and higher amounts of water to improve monomer impregnation into wet dentin substrate result in lower degree of polymerization of adhesive resin. These factors may also result in increased degradation [64-66].

Hybrid layer degradation might also stem from resin matrix degradation itself due to the differing monomer compositions of some currently used adhesive systems, besides breakdown of the hybrid layer as a consequence of intrinsic enzymatic activity. Since current adhesives used in combination with resin cements are composed of different meta-monomer matrices (methacrylate, methacrylamide-vinyl, styryl, allyl), variation in degradation levels can be expected. Methyl methacrylate (MMA) is one of the oldest monomers and is widely added to adhesives. Its function in adhesives is to dissolve other monomers [67]. Hydroxyethyl methacrylate (HEMA) is a type of small monomer that is widely used in dentistry. HEMA monomer is water soluble with low viscosity which enhances the solubility of the polar and non-polar adhesive components and the wetting behaviour of the liquid adhesive on the dental hard tissue. HEMA has also been described to be able to evaporate from the adhesive solutions, though only in very small amounts. Another important characteristic of HEMA is its hydrophilicity that makes it an excellent adhesion-promoting monomer by stabilizing the collagen fibril network and improving dentinal permeability and monomer diffusion. On the other hand, HEMA is not hydrolytically stable and concentrated solutions could promote its hydrolysis. Uncured HEMA (boiling point 198°C) is a fluid that is soluble in water, ethanol (boiling point 78°C) and/or acetone (boiling point 56-57°C) and thus an uncured monomer might cause allergic reactions. By enhancing wetting of dentin, HEMA significantly improves bond strength. Nevertheless, both in uncured and cured states, HEMA absorbs water [68].

bis-GMA, urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) are most frequently used cross-linkers in adhesive systems. Unlike mono-methacrylate monomers in adhesives, dimethacrylates' hydrophobic behaviour results in their limited solubility in water. This feature will also

prevent substantial water uptake after curing, with a consequence of discoloration of the adhesive resin [69]. On the other hand, adhesives that contain 10-methacryloxydecyl dihydrogen phosphate (10-MDP) as a bi-functional etching monomer can readily adhere to residual hydroxyapatite in the hybrid layer due to the dihydrogenphosphate group [68]. This bond was reported to be very stable [57,70]. Besides self-etching effect on dentin, specifically functional monomer 10-MDP has also chemical bonding efficacy by forming strong ionic bonds with calcium due to the low dissolution rate of the resulting Ca-salt in its own solution [57,68].

Although a complete encapsulation of the exposed collagen fibrils by resin is essential for a durable dentin bonding [71], primer and adhesive resin may incompletely penetrate the demineralized collagen network following etching in etch-and-rinse systems [72]. The discrepancy between depth of dentin demineralization following acid-etching and depth of resin infiltration results in incompletely infiltrated zones along the bottom of hybrid layer that contain denuded collagen fibrils [73,74]. Sano *et al* [73], described “nanoleakage” as the penetration of any substance into 20- to 100-nm-sized spaces present in the adhesive and/or tooth substrate throughout the hybrid layer and/or adhesive resin, and found that the location of defects under or within the hybrid layer at the resin-dentin interface could be the pathway for degradation of resin/dentin bonds over time. Silver nitrate is mainly used as a tracer for nanoleakage observation, and silver occupies nanometer-sized spaces around collagen fibrils, where resin fails to infiltrate, or where residual water has not been displaced by adhesive resin [72,75]. Transmission Electron Microscopy (TEM) images demonstrated that water can pass from dentin, around resin tags, to form water-filled channels that project from the hybrid layer into the overlying adhesive [63,76]. Different types of nanoleakage (spotted, reticular, water-treeing)

were described in *in vitro* aged specimens [15]. When these water-filled channels are stained with silver, they often look like microscopic trees termed as 'water-trees' that might act as potential sites for hydrolytic degradation of resin/dentin bonds. Thus far, all marketed products have permitted certain amount of nanoleakage and water-tree formation. Ideally, nanoleakage at the resin/dentin interface should be minimized or eliminated completely. Some techniques may be efficient in preventing nanoleakage. With ethanol-wet dentin bonding approach [77], by replacing ethanol with water in the primer, bisGMA/TEGDMA mixtures have been shown to infiltrate dentin, thus reducing nanoleakage and producing high bond strengths [78]. Self-etch adhesives do not require smear layer (which consists of bacteria, prepared tooth tissue particles that cannot be washed away, microbial dental plaque, saliva, etc.) removal by acidic conditioners and due to simultaneous etching and priming processes no discrepancy between the depth of demineralization and the depth of resin infiltration occurs [74]. However, it has been demonstrated that self-etch adhesive systems are also susceptible to nanoleakage within the hybrid layer [15]. If biodegradation of resin bonded dentin is to be avoided, complete penetration and polymerization of adhesive are essential. Additionally, the adverse effects of host-derived enzymes (esterases and matrix metalloproteinases) at the resin/dentin interface should be prevented [16].

Although phosphoric acid etching is effective in lowering collagenolytic activity by partial denaturation of the enzymes, some residual enzymatic activity still remains. If the resin poorly infiltrates, or if it slowly hydrolyzes and leaches from the hybrid layer, the intrinsic MMP activity of the dentin matrix can be expressed, causing it to dissolve [16,76]. This process weakens the hybrid layer, leading to shrinkage of dentin following cementation due to demineralization and dehydration processes and it eventually propagates biodegradation of hybrid layer leading to

nanoleakage/microleakage. Moreover, with occlusal forces loss of collagen and resin increases due to excessive fluid shear forces occurring in the voids under the compromised hybrid layer. On the other hand, once the collagen fibrils are completely covered by the resin, the effect of collagenolysis can be diminished [79].

The studies aiming to prevent biodegradation have focused on the use of MMP inhibitors in or with primers [80]. In 2005, Hebling *et al* [81] reported the anti-collagenolytic activity of chlorhexidine on host-driven enzymes (MMPs) in dentin. The authors suggested chlorhexidine use to inhibit the MMPs and to stop the self-destruction of the collagen matrices. In 2006, Tay and coworkers [82] conducted another study to test the inhibiting ability of chlorhexidine in collagen degradation and concluded the same results as Hebling *et al*, indicating that chlorhexidine was effective in inhibiting the collagenous enzymatic activity in dentin [81].

Hiraishi *et al*, conducted a study aiming to investigate the effect of pretreatment by chlorhexidine on the microtensile bond strength of resin cements and nanoleakage at the resin-dentin interfaces. They concluded that pretreatment with chlorhexidine affected the integrity of dentin bonding and that decreased the microtensile bond strength of resin cements at the resin-dentin interface [83]. Another study [84] investigating the effect of 0.2% and 2% chlorhexidine used as a therapeutic primer on the long-term bond strengths of two etch-and-rinse adhesive systems found increased nanoleakage during in vitro aging (thermocycling for simulating intraoral conditions, cyclic loading, etc.) in controls, but reduced silver deposits were found in chlorhexidine-treated specimens. The authors suggested that since no bacterial growth was present in the aging conditions and endogenous factors (MMP activity) thought to degrade the interface could be inhibited by chlorhexidine application on prepared dentin surfaces [84].

There are newer strategies for the elimination/minimization of nanoleakage at the resin/dentin interface by introducing some new chemical agents such as caffeic acid phenylethyl ester (CAPE), an active ingredient of propolis; however this material is still under further development stage for routine clinical use [85].

More recently, the influence of a new synthetic MMP inhibitor named '*galardin*' was evaluated on the proteolytic activity of dentinal MMPs and on the morphological and mechanical features of hybrid layers after aging. Galardin is a synthetic MMP-inhibitor with potent activity against MMP-1, -2, -3, -8 and -9 [84]. It has a collagen-like structure to facilitate binding to the active sites of MMPs and a hydroxamate structure ( $R-CO-NH-OH$ , where R is an organic residue) that chelates the zinc ion located in the catalytic domain of MMPs. However, the use of galardin was found to reduce the amount of nanoleakage, but failed to completely block biodegradation [84].

From a clinical point of view, resin-based adhesive luting cements require full penetration and polymerization, otherwise degradation will occur in time, causing nanoleakage in dentin and possibly caries formation under or around the margins of fixed-dental-prosthesis (FDP) as well as adhesively bonded restorations. However, degradation is a time-dependent phenomenon depending on the destruction of both collagen and hybrid layer, which makes time-dependent studies highly important from clinical point of view.

### **3. Restorative Materials**

#### **3.1 Metals**

A dental alloy, either base or noble, must fulfill certain minimum requirements for strength, stability, castability, corrosion/tarnish resistance, burnishability, polishability,

and biocompatibility to be considered successful. Metal-ceramic (ceramics supported by metal framework) alloys have additional requirements that are not usually essential for alloys used for full cast-metal restorations. Although esthetics may be supplied by the ceramic part of a metal-ceramic restoration, the success of the entire prosthesis depends largely on the physical properties of the metal substructure [86]. Higher melting temperature (over 1000°C), thermal compatibility with ceramics, oxide formation, and sag resistance are, therefore, required for a metal framework.

The gold-platinum-palladium (Au-Pt-Pd) alloys were the first to be used successfully for metal-ceramic restorations; however, their use decreased after more economical alloys (base and/or semi-precious, titanium metal alloys) were developed with significantly better mechanical properties and sag resistance. If the alloy contains more palladium than platinum, it is referred to as a gold-palladium-platinum alloy [87]. Alloys in which palladium has been eliminated are referred to as gold-platinum alloys. Because of their low sag resistance, the use of these alloys should be limited to crowns and three-unit fixed dental prosthesis (FDP). The Au-Pd alloys were developed to address the two main problems associated with silver-containing alloys: porcelain discoloration and a high coefficient of thermal expansion [87].

Due to low silver content in these alloys, porcelain does not discolor, castability is improved, and the coefficient of thermal expansion is increased [88]. Pd-Ag alloys were specifically developed to offer an economical alternative to more expensive gold-based alloys [89]. Pd-Ag alloys (coefficient of thermal expansion approximately ranging between  $14.6\text{--}17.1 \times 10^{-6}/^{\circ}\text{C}$ ) typically contain approximately 60% palladium, with the balance being silver and small amounts of indium and tin to facilitate the metal's oxide formation. High-palladium alloys were introduced in the 1980s, and were primarily developed for decreasing the material costs of noble alloys, to address

biocompatibility concerns of nickel-based casting alloys since nickel might cause allergic reactions, and to minimize the possibility of porcelain discoloration seen with Pd-Ag alloys [89]. For metal-ceramic use, base-metal alloys (nickel based and cobalt based) have been reported to have better castability than noble-metal alloys, but they tend to form thicker, darker oxide layers that may present esthetic problems [89]. Alloys in both systems contain chromium as their second largest constituent for corrosion resistance. They exhibit the highest modulus of any alloy type used for cast restorations [89].

The medical use of commercially pure titanium (cp Ti) and titanium alloys has increased significantly over the past 20 years. The successful use of titanium dental implants due to their biocompatibility has generated considerable interest in other dental uses for pure titanium and titanium alloys, including all-metal and metal-ceramic prostheses, as well as partial denture frameworks [91]. Titanium is considered to be the most biocompatible metal for a dental prosthesis [92].

### *3.2 Ceramics*

Ceramics, depending on their chemical composition, can be classified in three main categories: glass-ceramic, particle-filled glass, and polycrystalline [93].

#### *3.2.1 Glass-ceramic*

Dental ceramics that have high glass content best mimic the optical properties of enamel and dentin. Manufacturers use small amounts of filler particles to control optical effects such as opalescence, color and opacity. Ceramics containing high concentrations of leucite and lithium disilicate crystals are examples of glass-ceramics that are processed by injection-moulding.

The density change that occurs during firing of conventional feldspathic (a mineral with sodium, potassium or calcium content) porcelains or during the ceramming



procedure for castable glass-ceramics leads to undesired dimensional changes that result in inaccurate fit. Ceramming is a controlled crystallization (devitrification) of the glass that results in the formation of tiny crystals that are evenly distributed throughout the body of the glass structure. The size of the crystals, as well as the number and rate of growth is determined by the time and temperature of the ceramming heat treatment. There are two parts to the ceramming process; crystal nucleation and crystal growth. Each phase happens because the glass body is held at a specific temperature for a specific length of time. Press ceramic systems were attempted to overcome this effect by using glass-ceramic ingots. Pneumatic pressure injection of the molten glass-ceramic into a heated mold requires a special furnace capable of high temperatures. The dimensional change that occurs during solidification of the molten glass-ceramic is compensated by accurately matched expansion of the investment material. Pressable glass-ceramic systems, that replace the place left in the investment material after wax elimination, may be used for laminate veneers and complete crowns on anterior teeth and inlays, onlays, partial-coverage crowns and complete crowns on posterior teeth [94]. The flexural strength of a pressable glass-ceramic has been reported to increase subsequent to the high-temperature injection molding process, as well as following the glaze and/or enamel porcelain firing. The strength of this glass-ceramic material allows its use as an inlay, onlay and single crown restorative material [95].

### *3.2.2 Particle-filled glass*

Manufacturers add filler particles (silica, alumina, leucite, magnesia, etc.) to the base glass composition to improve mechanical properties, such as strength and thermal expansion and contraction behaviour. These fillers are usually crystalline, but they also can be particles of high-melting glasses that are stable at the firing temperatures

of the ceramic. The glassy matrix is selectively etched during hydrofluoric acid etching to create micromechanical retentive features enabling bonding. Particles can be added mechanically during manufacturing as powder or be precipitated within the starting glass by special nucleation and growth heating treatments; in the second case, such materials are termed "glass-ceramics" [96].

Another type of particle-filled glass is an alumina-based ceramic system where a two-phase core material is produced during a slip casting process and subsequently strengthened during a glass infiltration firing process [93]. The filler is alumina, magnesium aluminate spinel or a mixture of 70% alumina and 30% zirconia. Such an alumina based ceramic has been recommended for single anterior and posterior crowns, as well as for anterior three-unit FDPs [93].

The core is trimmed and built to anatomical contour using conventional techniques with dentin and enamel porcelain. The superior fit of alumina-based ceramic crowns is attributed to low-temperature sintering of the core material, which results in minimal volumetric shrinkage and excellent marginal adaptation [88]. Although the alumina core has high strength, it is characteristically opaque. Incorporating magnesium aluminate spinel rather than aluminum oxide, results in improved optical properties characterized by increased translucency with only small reduction in flexural strength [93,97].

### *3.2.3 Polycrystalline ceramics*

*Polycrystalline ceramics* do not contain glass; the matrix is aluminum oxide or zirconium oxide, and the fillers are not particles but modifying atoms called "dopants." All of the atoms are packed into regular crystalline arrays, preferably tetragonal, through which it is much more difficult to drive a crack than in atoms in the less dense and irregular network found in glasses; therefore, polycrystalline ceramics generally

are much tougher and stronger than glass-based ceramics. Highly esthetic dental ceramics with improved colour and translucency have high glass content, and higher-strength substructure ceramics generally are crystalline. The historical development of substructure ceramics has involved an increase in crystalline content ranging from approximately 55% crystalline to fully polycrystalline [98].

At the beginning of the 1990s oxide ceramics that contain only little or no silica were introduced into restorative dentistry. Oxide ceramics (e.g. zirconium dioxide and aluminum oxide) contain less than 15 wt% silica and only a small or no glass phase [99]. Dental oxide ceramics were first glass-infiltrated or densely sintered alumina ceramics, followed by zirconia reinforced glass-infiltrated alumina ceramic, and since then, several densely sintered zirconia ceramic systems have been introduced [100]. Current dental oxide ceramics consist mostly of alumina, magnesia, zirconia or yttria. Because of their high strength, oxide ceramics are used as frameworks and for replacing alloys not only in crowns but also in multiple-unit FDPs. In addition, because of their high strength, adhesive luting techniques are not required for oxide ceramic dental restorations as the abutment teeth provide adequate mechanical retention (ideally 6-8° axial taper of the prepared tooth) for conventional cements. Nevertheless, adhesive luting techniques for oxide ceramics, because of the strength of both the adhesive and the ceramic, can provide significant clinical advantages over conventional cementation of dental restorations [99]. Adhesive luting with light-curing, dual-curing or self-curing cements can provide sealed restoration margins, minimizing microleakage and, thereby, reducing secondary caries risk [96]. Esthetics might also be improved by using tooth colored and/or transparent resin luting agents as compared to opaque conventional cements, and tooth colored restorative

materials, like ceramics or composite resins, can be bonded to the teeth without visible cementation line [101].

Computer-aided systems use a 3D data set representing either the prepared tooth or a wax model of the desired framework. Such systems use this 3D data set to create an enlarged die upon which ceramic powder is condensed or to machine an oversized part for firing by machining blocks of partially sintered ceramic powder [96].

All-ceramic restorations combining esthetic veneering porcelains with strong ceramic cores (such as zirconia, lithium disilicate, alumina) have become popular. Veneering porcelains typically consist of a glass and a crystalline phase of fluoroapatite, aluminum oxide, or leucite. Veneering a lithium disilicate, aluminium oxide, or zirconium oxide core with glass allows dental technicians to customize these restorations in terms of form and esthetics. The most commonly reported major clinical complication resulting in failure of all-ceramic restorations is the fracture of the veneering porcelain and/or the framework [102]. The success of these systems depends on preventing failure by retarding crack propagation by arresting the cracks induced by masticatory loading inside the inherently brittle ceramic material through reinforcement with high-performance core (framework) ceramics such as alumina, zirconia and lithium disilicate. The use of all-ceramic systems for FDPs has limitations. A minimum FDP connector height of 3 to 4 mm from the interproximal papilla to the marginal ridge is a prerequisite for most systems. When there is reduced interocclusal distance, short clinical crowns, deep vertical overlap or an opposing supraerupted tooth, cantilevers, periodontally involved abutment teeth, and patients with severe bruxism or parafunctional activity, their use is contraindicated [103]. The primary cause of failure varies from fracture of the connector for aluminium oxide/lithium disilicate FDPs to cohesive fracture of the veneering porcelain for

zirconia FDPs [104]. However, metal-ceramic FDPs mainly fail due to tooth fracture and caries [94,105].

Due to high content of silica in silica-based ceramics, organosilanes have been successfully used to promote the bond between the silica ceramic and the resin-based luting cement usually after roughening the ceramic surface by hydrofluoric acid etching or airborne particle abrasion. Organosilanes are organofunctional trialkoxysilanes or silane esters containing a non-hydrolysable organic group and a hydrolysable group and they have a dual reactivity. The non-hydrolysable functional group with a carbon-carbon double bond polymerizes with monomers containing double bonds. The hydrolysable alkoxy group reacts with the ceramic surface rich in hydroxyl groups. [96,106-109].

Adhesion among the prepared tooth surface, composite luting resin and the restoration assembly requires adhesive bonding of each surface to each other. This can be achieved through surface modifications of the tooth and restoration surfaces and using an adhesive luting cement to combine these dissimilar materials. Adhesive bonding of oxide ceramics allows the introduction of new non-invasive treatment choices for tooth replacement by resin bonding all-ceramic FDPs. Conventional mechanically retentive tooth preparation can be considered invasive since sound tooth structure is usually removed [99]. Adhesive luting, on the other hand, does not require such a mechanical retention, and adhesion through chemical bonding is sufficient. However, bonding methods used for conventional silica-based dental ceramics are not suitable for dental oxide ceramics. Densely sintered alumina and zirconia ceramics offer similar bonding substrates in a way that they are both completely free of glassy phase with grains sintered into a dense and homogeneous structure. Chemically, their surfaces consist mainly of either aluminum oxide or

zirconium dioxide to which specific bi-functional monomers bond well [110,111]. Oxide ceramics cannot be efficiently etched with hydrofluoric acid for resin bonding [100,112] and although the most often used coupling agent for silica-based ceramics, 3-methacryloxypropyltrimethoxysilane (MPS), might help in surface wetting of oxide ceramics, it does not promote adequate bonding to alumina or zirconia ceramics [99,113]. The silanes should be first hydrolysed (pre-activated) for formation of silanols that are adsorbed, deposited and polymerized on the substrate surface followed by hydrogen bond and covalent Si-O-Si bond formation, called silanization. This process promotes the adhesion between the etched silica containing dental ceramic surface (hydroxyl group) and the composite resin through silanes. Therefore, alternative bonding techniques must be developed for dental oxide ceramics.

Adhesion to mainly non-precious dental metal surfaces, especially in resin-bonded FDPs, where major retention has been achieved through metal “wings” covering the palatal surfaces of the teeth together with a resin composite luting cement, can also be enhanced by silica coating and subsequent silanization of the cementation surfaces [114].

### *3.3. Composites*

The physical, mechanical and esthetic properties and the clinical behaviour of composites depend on their structure. Dental composites are composed of three chemically different materials: the organic matrix (organic phase), inorganic matrix, filler or disperse phase, and an organosilane or coupling agent to bond the filler to the organic resin. This agent is a molecule with silane groups at one end, and methacrylate groups at the other for covalent bonding with the resin. Basically, the organic matrix of the composite resins is made up of a system of mono-, di- or tri-functional monomers; a free radical polymerization initiation system, which in

photocurable composite resins is an  $\alpha$ -diketone (camphoroquinone) used in combination with a tertiary aliphatic amine reducing agent (4-N,N-dimethylamino-phenyl-ethanol, DMAPE). In chemically-curing systems, initiation system is a benzoyl peroxide, used in combination with an aromatic tertiary amine (N,N-dihydroxyethyl-p-toluidine) and an acceleration system (dimethylaminoethyl methacrylate or DMAEM, ethyl-4-dimethylaminobenzoate or EDMAB, or N,N-cyanoethyl-methylaniline or CEMA), which acts on the initiator, allowing curing to take place. In addition, a stabilizer or inhibitor system such as hydroquinone monomethyl ether maximizes the shelf-life of the product before curing and increases its chemical stability. The absorbers of ultra-violet wavelengths below 350 nm, such as 2-hydroxy-4-methoxybenzophenone, provide colour stability and eliminate the effects of UV light on the amine compounds in the initiator system that can cause discoloration in the medium to long term because of its inherent color instability due to temperature changes and storage conditions [115].

The monomer system (bis-GMA) can be viewed as the backbone of the composite resin system, although not the major component. bis-GMA is still the most used monomer for fabricating composites; whether alone or in conjunction with urethane dimethacrylate, it constitutes around 20% (v/v) of composite resin composition. It is accepted that the lower the mean molecular weight of the monomer or monomer combination, the higher the percentage of shrinkage.

Since bis-GMA is highly viscous, it is diluted with other low-viscosity monomers (low molecular weight) which are considered viscosity controllers, such as bisphenol A dimethacrylate (bis-DMA), ethylene glycol dimethacrylate (EGDMA), triethylene glycol dimethacrylate (TEGDMA), methyl methacrylate (MMA) or urethane dimethacrylate (UDMA) to facilitate the fabrication process and clinical handling

[116]. bisphenol-A, a component in composite resins, alone might be toxic; however no free, unreacted BPA in bis-GMA or bis-DMA has been reported in dental composite resins. Besides, to liberate the BPA from these resins, temperature exceeding several hundred degrees is required. Moreover, measurements on exposure to BPA from dental resins revealed potential doses that are hundreds or thousands of times less than any known toxic level [117]. The disperse phase of composite resins is made up of an inorganic filler material that basically determines the physical and mechanical properties of the composite. The nature of the filler, how it is obtained and how much it is added largely decide the mechanical properties of the restoration material. The filler particles are added to the organic phase to improve the physical and mechanical properties of the organic matrix, so incorporating a high percentage of filler as much as possible is a fundamental objective. The filler reduces the thermal expansion coefficient and overall curing shrinkage, provides radio-opacity, improves handling and optical properties of resin composites [118,119].

The filler particles used vary widely in their chemical composition, morphology and dimensions. The main filler is silicon dioxide; boron silicates and lithium aluminium silicates are also commonly employed. In many composites, the quartz is partially replaced by heavy metal atoms such as barium, strontium, zinc, aluminium or zirconium, which are radiopaque as well. Current materials involve calcium metaphosphate, that is less hard than glasses and, therefore, cause less wear on the opposing tooth [120].

Nanotechnology has led to the development of new composite resins containing nanoparticles approximately 25 nm and nanoaggregates of approximately 75 nm, which are made up of zirconia/silica or nanosilica particles (filler). The aggregates are treated with silane for binding to the resin [121].



#### **4. Adhesion Test Methods in Dentistry**

In dentistry, the strength of a material and the strength of the union of dissimilar materials are tested through various adhesion test methods. Two main types of strengths have been reported: tensile and shear that result from pure loading modes. Other test systems are combinations of these two methods. [122].

Some fundamental aspects of adhesion were investigated in a recent review article [123], and these aspects were related to dental adhesion studies. The results of that research revealed that the meaning of the overall adhesion strength value as usually defined in dentistry does not conform to the meaning in fields such as mechanical engineering and physics. Adhesion studies in dental medicine should approach the problem from fracture mechanics and fatigue points of view rather than from an overall strength point of view. If no strong evidences correlating clinical success with any particular adhesion test method are present, in vitro tests should not be used as predictors of clinical performance [123].

Current approach in dental materials testing is to load multiple test specimens from each tooth in either a tensile (microtensile bond strength) or shear (microshear bond strength) bond strength testing configuration. Results generated from primarily shear and microtensile tests are commonly used when different products are being marketed, so this might misleadingly give an impression that higher bond strength results in better clinical performance.

Smaller sized test specimens are deemed stronger than larger sized specimens due to the lower probability of having a critical sized defect present and aligned in a crack opening orientation relative to the applied load [124].

#### *4.1. Microshear Bond Strength Test*

Shear bond strength (SBS) test with bonded cross-sectional areas of 1 mm<sup>2</sup> or less is referred to as microSBS ( $\mu$ SBS) [125]. This relatively simple test permits conservation of extracted tooth tissues by controlled, slow cross-sectioning process under cooling. Moreover, regional bond strength depending on the orientation of dentin tubuli is achieved through small cross-sectional area bond strength testing. A significant advantage over microtensile ( $\mu$ TBS) methods is that the  $\mu$ SBS specimen is prestressed before testing only by mould removal. However, the use of the mould for placement can lead to the introduction of flaws and different stress concentrations resulting from shear loading, similar to macroSBS methods [123].  $\mu$ SBS tests are suitable for substrates such as glass ionomers or enamel, in terms of specimen preparation effects and test conditions of  $\mu$ TBS testing.

#### *4.2. Microtensile Bond Strength Test*

The microtensile bond strength is calculated as the tensile load at failure divided by the cross-sectional area of the bonded interface. However, this is valid only if a state of uniform, uniaxial stress is present [126,127] with the maximum tensile stress present and homogeneously distributed in the region of the bonded area [128].

Advantages of  $\mu$ TBS test are conservation of teeth, evaluation of regional bond strengths [129,130], evaluation of intra- and inter-tooth variability, more uniform loading due to less bending offset relative to conventional tensile testing, fewer cohesive failures in substrates, higher bond strengths than those from conventional tensile and shear bond strength tests due to the decreased number of defects in the substrate or at the bonded interface [131], possibility to evaluate very small surface areas when necessary, minimizing the shear effect by tensile testing a relatively flatter region of tooth. However, limitations of  $\mu$ TBS test method include: technique

sensitivity, difficulty in measuring very low bond strength (<5 MPa), ease of dehydration and damage of extracted tooth specimens, loss or damage of specimens when removing from active jigs that use glue and difficulty in fabrication with consistent geometry [124].

Specimen geometry and preparation effects as well as test speed are also parameters contributing to the variations in test methodologies [112]. No agreement has been reached favoring a particular strength test method regarding its clinical correlation, yet. Too many variables are involved in bond testing, and because of interactions between these variables, it is difficult or impossible to compare results from different studies. Even when the same batches and the same experimental conditions are used, significant variations still exist among findings of same researchers [132]. Considering all these variations it can be stated that bond strength data resulting from different groups or individuals are far from being reproducible [133,134]. The reason is that the measured bond strength values neglect the true stress distribution [135] and that the results are highly affected by defects introduced during sample preparation [132-136]. It is suggested that fracture mechanics approaches should be used instead of using strength testing approaches, and using fracture mechanics the impact of crack formation and crack propagation on the clinical behavior should be investigated. Neither microtensile nor shear bond test uses fracture mechanics to solve the adhesion testing problem. However, when tensile and shear tests are compared, there is a distinct difference between these two methods in that the application of the force affects the opening mode of the joint. Even though it might seem that the failure occurs instantaneously over the entire bond area when the adhesive joint fails, the crack starts propagating from an edge and rapidly propagates along the interface [123,124-128]. Factors such as stress

concentration at the crack tip and the rate with which energy stored in the stressed system recovers are the main factors that should be considered. Fracture mechanics tests, in contrast to strength tests, consider localized stress concentration factor, and the energy release rate [124]. An extensive review of methodologies for adhesion tests used for teeth and restorative materials in dentistry could be helpful for the reader [137].

## **5. Future Perspectives and Expectations**

The initiation of hybrid layer degradation, whether from the adhesive or the dentin side, remains unclear. No matter where biodegradation starts, our main approach should be, with today's knowledge, to use non-hydrolysing polymers and inhibit enzymatic activity in dentin.

While technique-sensitive adhesive systems are being simplified in terms of application steps, no compromise should be made in terms of pivotal properties for stable adhesion.

In order to meet increased esthetic demand in recent years, with the necessity for minimally invasive treatment modalities, durable materials should be adopted in a conservative treatment approach.

Adhesion research on dental substrates and materials requires long-term clinical data and standardization of test methods.

## **6. Conclusions**

1. With etch-and-rinse as well as self-etch adhesive systems, durable adhesion can be achieved on enamel due to its high mineral content and less organic matrix.

2. The long-term durability of dentin bonding is of vital importance for clinical success, besides the initial bond strength of an adhesive to dentin. Focus should be on the preservation of the hybrid layer and inhibition of biodegradation.
3. Nanotechnological developments in ceramics, polymers, dental resin composites and metals would enhance the physical, chemical and optical properties of materials as well as their malleability and would save time for chairside and/or laboratory fabrication procedures.
4. Traditional strength test methodology lacks true interpretation of adhesion data in dental science, and in vitro tests alone should not be used as predictors of clinical performance. If we can develop new dynamic test methods for correlating results on long-term performance of new materials in dentistry, only then in vitro test methods will have a practical meaning.
5. Optimal bond strength related to local stress distributions generated during adhesion testing of dental materials should be well understood before bond strength testing can be standardized.

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